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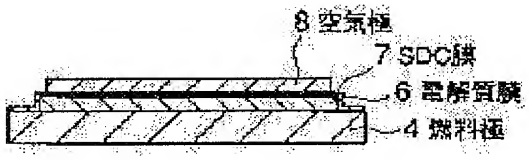
(54) UNIT CELL FOR SOLID ELECTROLYTIC FUEL BATTERY AND ITS MANUFACTURING METHOD

(57)Abstract:
PROBLEM TO BE SOLVED: To provide a unit cell for a solid electrolytic fuel battery which has a high power generation performance.
SOLUTION: A layer of SDC(samara-doped ceria) or the like is at least set between an electrolyte film and an air pole. By the setting of the SDC layer, an electrical resistance can be reduced between the electrolyte film and the air pole, and a unit cell with a high power generation performance can be obtained.



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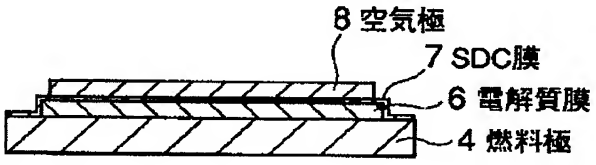
(54)【発明の名称】　固体電解質型燃料電池の単電池、およびその製造方法

(57)【要約】
【課題】　発電性能の高い固体電解質型燃料電池の単電池を提供する。
【解決手段】　少なくとも電解質膜と空気極との間にＳＤＣ（サマリアをドープしたセリア）などの層を設けることとした。ＳＤＣの層を設けることにより電解質膜と空気極との電気抵抗を低減でき、発電性能が高い単電池を得ることができる。



【特許請求の範囲】
【請求項１】　燃料極を基板とし、該燃料極の上に電解質膜を形成し、該電解質膜の上に空気極を形成し、前記空気極に酸化剤ガス、前記燃料極に燃料ガスを供給し、両者間で起電力を発生させて電力を得る固体電解質型燃料電池の単電池において、
前記電解質膜と前記空気極との間にＣｅ1-X ＦX Ｏ(2-δ)の膜（ＦはＣａ、Ｙ、Ｓｍ、Ｇｄ、Ｌａ、Ｍｇ、Ｓｃ、Ｎｄ、Ｙｂ、Ｐｒ、Ｐｂ、Ｓｒ、Ｅｕ、Ｄｙ、Ｂａ、Ｂｅのいずれか１つ又は２つ以上の組合せであり、０≦ｘ≦０．５０）を形成したことを特徴とした固体電解質型燃料電池の単電池。
【請求項２】　前記Ｃｅ1-X ＦX Ｏ(2-δ)の膜を、前記燃料極の表面全体に形成したことを特徴とする請求項１記載の固体電解質型燃料電池の単電池。
【請求項３】　前記Ｃｅ1-X ＦX Ｏ(2-δ)の膜は、サマリアをドープしたセリア膜であることを特徴とする請求項１または２記載の固体電解質型燃料電池の単電池。
【請求項４】　前記電解質膜は、印刷法を用いて前記燃料極に形成したことを特徴とする請求項１～３のいずれか１項に記載の固体電解質型燃料電池の単電池の製造方法。
【請求項５】　前記印刷法は、スクリーン印刷法である請求項４に記載の固体電解質型燃料電池の単電池の製造方法。
【発明の詳細な説明】
【０００１】
【発明の属する技術分野】本発明は、燃料極を支持体として構成した支持膜型の固体電解質型燃料電池の単電池に関し、特に発電性能を向上させた固体電解質型燃料電池の単電池に関する。
【０００２】
【従来の技術】固体電解質型燃料電池の単電池は、電解質の一方の面に空気極を設け、他方の面に燃料極を設けてあり、固体電解質型燃料電池はこのような単電池を複数積層し、空気極に酸化剤ガスを、燃料極に燃料ガスを供給して起電力を発生させている。
【０００３】次に、ディップ法を用いた支持膜式の単電池の製造方法について、図１２に示す流れ図を用いて説明する。
【０００４】まず粉末状の燃料極の原料をプレスにより所定の形状に押し固め成形し（Ｔ１）、成形した燃料極（グリーン）を電気炉等により約１００時間仮焼し、多孔体とする（Ｔ２）。次に、仮焼した燃料極を、電解質の原料をスラリ状にした電解質スラリの中に浸し（Ｔ３）、燃料極の表面全体に薄く電解質原料を付着させる。電解質スラリを付着させたなら、電解質スラリを適度に乾燥させ（Ｔ４）、再び燃料極を電解質スラリの中に浸し、電解質原料を表面に付着させ、再度乾燥を行なう。このような電解質原料の付着・乾燥作業を電解質原料が所定の厚みとなるまで（７回程度）繰り返し、電解質膜が燃料極の表面に所定の厚みに形成されたなら炉に入れ焼成（Ｔ５）する。
【０００５】次に電解質膜を研磨し、燃料極の周囲に形成された不要な電解質膜を除去して、所定の形状に仕上げる（Ｔ６）。そして、電解質膜の上に空気極を設け（Ｔ７）、焼成を行なっていた（Ｔ８）。
【０００６】このようにして従来は、電気的抵抗が高い電解質膜を１０～数１０μｍの薄膜として抵抗を低減させ、単電池の作動温度を低くして、固体電解質型燃料電池の単電池のコストや熱機械的信頼性等を向上させていた。
【０００７】
【発明が解決しようとする課題】しかしながら、近年固体電解質型燃料電池は小型化、高出力化を図る必要があり、より高い発電性能が単電池に求められている。例えば、電解質膜と空気極、あるいは電解質膜と燃料極との間の電気抵抗をより低減させ、より高い発電性能を実現することが求められている。
【０００８】
【課題を解決するための手段】本発明では、上記課題を解決するため、単電池を次のようにして構成した。
【０００９】すなわち、電解質膜と空気極との間にＳＤＣ（サマリアをドープしたセリア）の層（膜）などＣｅ1-X ＦX Ｏ(2-δ)の膜（ＦはＣａ、Ｙ、Ｓｍ、Ｇｄ、Ｌａ、Ｍｇ、Ｓｃ、Ｎｄ、Ｙｂ、Ｐｒ、Ｐｂ、Ｓｒ、Ｅｕ、Ｄｙ、Ｂａ、Ｂｅのいずれか１つ又は２つ以上の組合せであり、０≦ｘ≦０．５０）を形成して単電池を構成した。
【００１０】その塗布方法は例えば、燃料極の上に電解質膜を形成した段階で、電解質膜の上にＳＤＣのスラリ等を塗布し、そののち空気極を電解質膜の上に形成することとした。これにより、電解質膜と空気極との間の電気抵抗を低減でき、発電性能の高い単電池を得ることができる。ＳＤＣ膜等は、少なくとも電解質膜側の面に塗布すればよいが、電解質膜を形成した面の裏面の燃料極表面に塗布してもよい。
【００１１】
【発明の実施の形態】本発明にかかる単電池の一実施例について説明する。
【００１２】図１に単電池２を示す。単電池２は、支持体としての燃料極４の表面に電解質膜６が形成してあり、さらに電解質膜６の表面にＳＤＣ膜７を介在させて空気極８が形成してある。この単電池２を図１０に示すように合金セパレータ３０とセラミックマニホールド３２からなるセパレータ３４で挟持し、セパレータ３４と単電池２とを適宜積層して固体電解質型燃料電池１が構成してある。固体電解質型燃料電池１は、所定の条件（例えば温度７５０℃等）において燃料極４に燃料ガスを、また空気極８に酸化剤ガスを供給することにより起

電力を発生する。

【００１３】次に、単電池２の製造方法について図７の流れ図を用いて説明する。まず、粉末状の原料を所定の形状に成形し、支持体としての燃料極４を形成する（Ｓ１）。燃料極４の原料は、例えばニッケルとイットリア安定化ジルコニア（ＹＳＺ）のサーメットであり、原料を水溶性のバインダ、例えばポリビニルアルコールと混練し、プレス装置（図示せず）等により押し固め、成形する。所定の形状に成形した燃料極４を図３に示す。燃料極４の原料には、造孔剤（図示せず）が所定量含有してあり、後述する焼成により造孔剤が焼失されると燃料極４の内部に多数の孔が形成される。

【００１４】プレス装置により成形された未焼成の燃料極４は、そのままの状態で塗布装置１８（図２参照）に配置され、電解質スラリ２４が表面に塗布される（Ｓ２）。電解質スラリ２４は、ＹＳＺからなる電解質（電解質膜６）の原料と非水溶性のバインダ、例えばポリビニルブチラールとを混練したものであり、所定の粘度に設定してある。尚、バインダとしては、上記以外に、メチルセルロース、ポリエチレン、ポリアクリル酸ソーダ、アラビアゴムなどがある。

【００１５】図２に示すように塗布装置１８は、いわゆるスクリーン印刷法で印刷を行なう印刷機であり、スクリーン版２０には電解質膜６に等しい形状の型が形成されている。燃料極４を、塗布装置１８の所定の位置に配置したなら、スクリーン版２０に沿ってスキージ２２を移動させることにより、型を通して電解質スラリ２４が燃料極４の上面に塗布（Ｓ２）される。電解質スラリ２４が所定の形状に塗布されたなら、電解質の表面を適宜乾燥させる。乾燥作業は、電解質スラリ２４を完全に乾燥させる必要はなく、塗布した電解質スラリ２４上に重ねて電解質スラリ２４が塗布できる程度であればよい。電解質膜６が表面に形成された燃料極４を図４に示す。

【００１６】電解質スラリ２４を適度に乾燥させたなら、上記と同様にして重ねて電解質スラリ２４を塗布し、乾燥させる。そして電解質スラリ２４が所定の厚さになるまで電解質スラリ２４の塗布を繰り返す。電解質スラリ２４が所定の厚みに積層されたなら、燃料極４とともに共焼結（電解質膜６と燃料極４とを一緒に焼成すること）する（Ｓ３）。

【００１７】そして、電解質膜６にＳＤＣを塗布して、ＳＤＣ膜７を形成する。ＳＤＣは、サマリアをドープしたセリア（$Ce_{1-x}Sm_xO_{(2-\delta)}$）であり、粒径が０．１～５μｍ程度で、ｘ＝０．３である。ＳＤＣは、その粉末をＣｅゾルに分散、混合してＳＤＣスラリを形成し、ディップ法等により電解質膜６の表面全体に４μｍの厚さに塗布する（Ｓ４）。ＳＤＣ膜７が塗布された状態を図５に示す。次に塗布したＳＤＣ膜７を所定の温度で焼成する（Ｓ５）。焼成したなら、空気極８をＳＤＣ膜７を介して電解質膜６の上に塗布し（Ｓ６）、全体を焼成して完成させる（Ｓ７）。空気極８は、平均粒径が０．６０μｍの$La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_3$と、この粒子の周囲を取り囲む粒径が０．１μｍの$Ce_{0.8}Sm_{0.2}O_{1.9}$の組成を有する粒子（ＬＳＣＦ－ＳＤＣ）からなり、$Ce_{0.8}Sm_{0.2}O_{1.9}$は０．５～６０ｗｔ％含まれている。空気極８を電解質膜６の上に形成した単電池２の全体を図６に示す。

【００１８】尚、空気極８は、$(A_{1-x}B_x)(C_{1-y}D_y)O_{(3+\delta)}$の組成を有する粒子と、$Ce_{1-X}E_XO_{(2-\delta)}$の組成を有する粒子（ＡはＬａ、Ｙ、Ｓｍ、Ｇｄ、Ｐｒ、Ｃａのいずれか１つ又は２つ以上の組合せ、ＢはＳｒ、Ｂａ、Ｃａのいずれか１つ又は２つ以上の組合せ、ＣはＭｎ、Ｃｏ、Ｃｅのいずれか１つ又は２つ以上の組合せ、ＤはＣｒ、Ｎｉ、Ｍｇ、Ｚｒ、Ｃｅ、Ｆｅ、Ａｌのいずれか１つ又は２つ以上の組合せ、ＥはＣａ、Ｙ、Ｓｍ、Ｇｄ、Ｌａ、Ｍｇ、Ｓｃ、Ｎｄ、Ｙｂ、Ｐｒ、Ｐｂ、Ｓｒ、Ｅｕ、Ｄｙ、Ｂａ、Ｂｅのいずれか１つ又は２つ以上の組合せであり、$0 \leqq x \leqq 0.50$、$0 \leqq y \leqq 0.50$）とから構成すればよく、また$(A_{1-x}B_x)(C_{1-y}Dy)O_{(3+\delta)}$の組成を有する粒子は、径が０．１～２０μｍ、$Ce_{1-X}E_XO_{(2-\delta)}$の組成を有する粒子は、径が０．１～５μｍであればよい。

【００１９】更に電解質膜６と空気極８との間にはＳＤＣ膜７でなく、$Ce_{1-X}F_XO_{(2-\delta)}$の膜（ＦはＣａ、Ｙ、Ｓｍ、Ｇｄ、Ｌａ、Ｍｇ、Ｓｃ、Ｎｄ、Ｙｂ、Ｐｒ、Ｐｂ、Ｓｒ、Ｅｕ、Ｄｙ、Ｂａ、Ｂｅのいずれか１つ又は２つ以上の組合せであり、$0 \leqq x \leqq 0.50$）を形成してもよい。またその粒径は０．１～２μｍ程度であればよい。更に、酸素分圧やそれぞれの膜の熱膨張の差などの観点から、電解質膜６とＳＤＣ膜７等との膜厚の比率は、実質的に１０以上であればよい。

【００２０】このように、電解質膜６と空気極８との間に導電性の高いＳＤＣ膜７を設けたことにより、空気極８と電解質膜６との界面の電気抵抗が低減され、高い発電性能を得ることができる。また、スクリーン印刷法を用いて電解質膜６を形成したことにより表面に凹凸が形成され、電解質膜６と空気極８との間の接触面積が増大し、密着性が向上する。

【００２１】さらに、支持体である燃料極４に所定の形状、厚みの電解質膜６を簡易、迅速に塗布、形成することができ、また、燃料極４を仮焼することなく、燃料極４の原料を成形した後直接電解質スラリ２４を燃料極４に塗布できることから、手間とコストを大幅に削減することができる。また、スクリーン版２０を通過させて電解質スラリ２４を塗布することから、適度な凹凸が形成され、良好な電解質膜６を形成することができる。

【００２２】また、燃料極４と電解質スラリ２４それぞれのバインダの性質、すなわちバインダが水溶性か非水溶性かの組み合わせを適宜選択することにより、燃料極４に電解質スラリ２４を塗布した際の両者間に形成され

る界面の状態を調整でき、焼成した後緻密で、不純物の少ない良好な電解質膜６を形成できる。更に、両者のバインダを水溶性か非水溶性か等の組み合わせ以外の組みあわせで適宜選択することにより電解質膜６の表面や電解質膜６と燃料極４の界面を所望の構造にすることができる。

【００２３】尚、ＳＤＣ膜７は、電解質膜６の全体表面でなく、図８および図９に示すように、燃料極４と電解質膜６の外表面全体に塗布してもよい。また空気極８は従来の空気極でよく、空気極８を電解質膜６の上に形成する製造方法も従来どおりでよい。

【００２４】尚、上記例ではスクリーン印刷法によって電解質スラリを塗布して電解質膜を形成することとしたが、本発明では、スクリーン印刷に限らず、他の印刷法でもよく、更にディップ法により電解質膜を形成してもよい。

【００２５】またバインダの性質は、上記例に限らず他の種類の組み合わせでもよい。

【００２６】実験例

図１１に本件発明にかかる実験結果を示す。実験に用いた単電池は、燃料極をＮｉとＹＳＺのサーメット、電解質をＹＳＺ、空気極を平均０．６μｍの（Ｌａ１－ｘＳｒｘ）（Ｃｏ１－ｙＦｅｙ）Ｏ（３＋δ）粒子（ｘ＝０．４、ｙ＝０．２）と、０．１μｍのＣｅ１－ｘＳｍｘＯ（２－δ）粒子（ｘ＝０．２）から構成し、燃料極に電解質膜を形成した状態で、一方は全体に、他方は電解質膜と空気極の間にのみＳＤＣ（Ｃｅ０．７Ｓｍ０．３Ｏ（２－δ））膜を設け、それぞれ空気極をＳＤＣ膜の上に形成した。

【００２７】これら単電池を、７５０℃の作動温度で、燃料ガスと酸化剤ガスとを供給し、発電を開始させ、電流密度に対する電圧を計測した。これにより、電流密度が上昇しても電圧の降下が少なく、高い発電性能が得られ、しかもＳＤＣ膜を燃料極と電解質膜との間のみでなく電解質膜の逆側、すなわち燃料極の表面側にも形成した方が良い結果が得られることがわかる。

【００２８】

【発明の効果】本発明の単電池によれば、少なくとも電解質膜と空気極との間にＳＤＣ膜などＣｅ1-χ ＦＸ Ｏ(2-δ)の膜（ＦはＣａ、Ｙ、Ｓｍ、Ｇｄ、Ｌａ、Ｍｇ、Ｓｃ、Ｎｄ、Ｙｂ、Ｐｒ、Ｐｂ、Ｓｒ、Ｅｕ、Ｄｙ、Ｂａ、Ｂｅのいずれか１つ又は２つ以上の組合せであり、０≦ｘ≦０．５０）を形成したことにより、電解質膜と空気極との電気抵抗を低減し、高い発電性能の単電池を得ることができる。

【図面の簡単な説明】

【図１】本発明にかかる単電池を示す図である。

【図２】塗布装置を示す図である。

【図３】燃料極を示す図である。

【図４】電解質膜を形成した燃料極を示す図である。

【図５】ＳＤＣ膜を形成した燃料極を示す図である。

【図６】単電池を示す図である。

【図７】本発明にかかる製造方法の手順を示す図である。

【図８】ＳＤＣ膜を形成した電解質膜と燃料極の断面図である。

【図９】ＳＤＣ膜を形成した単電池を示す断面図である。

【図１０】固体電解質型燃料電池を示す図である。

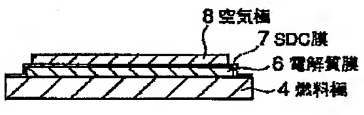
【図１１】実験結果を示す図である。

【図１２】従来の製造方法の手順を示す図である。

【符号の説明】

２　単電池
４　燃料極
６　電解質膜
７　ＳＤＣ膜
８　空気極
１８　塗布装置
２０　スクリーン版
２２　スキージ
２４　電解質スラリ
３０　合金セパレータ
３２　セラミックマニホールド
３４　セパレータ

【図１】



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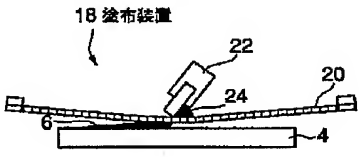

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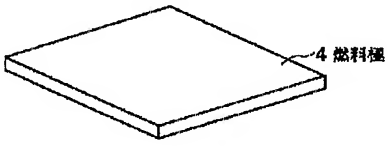
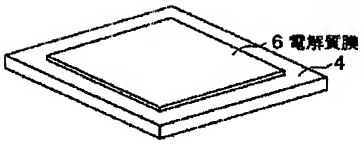


【図８】

【図４】



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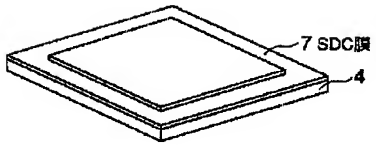

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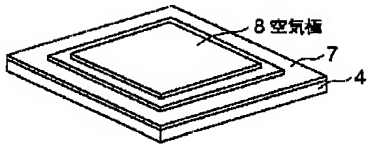

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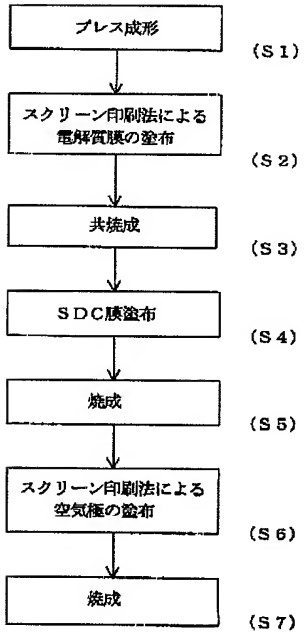

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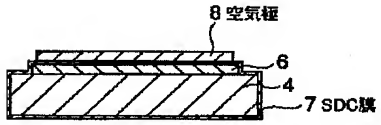

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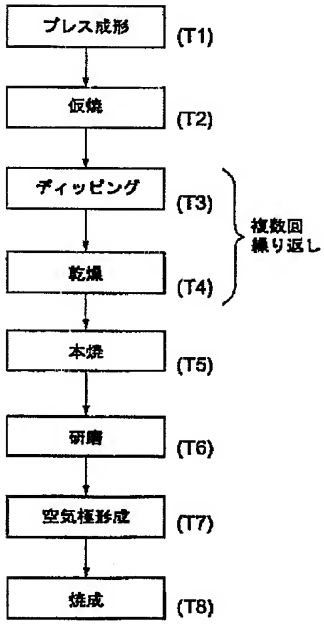

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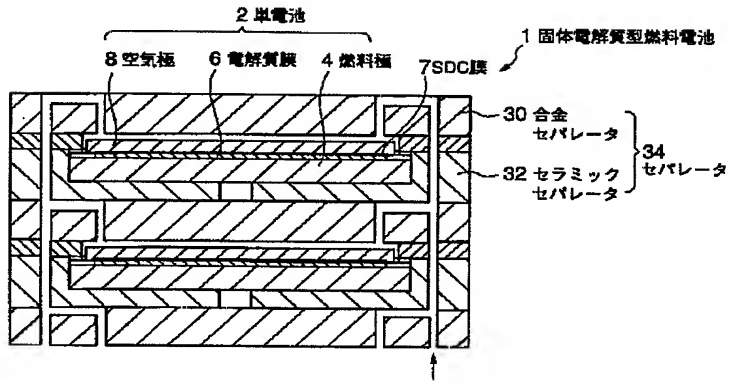

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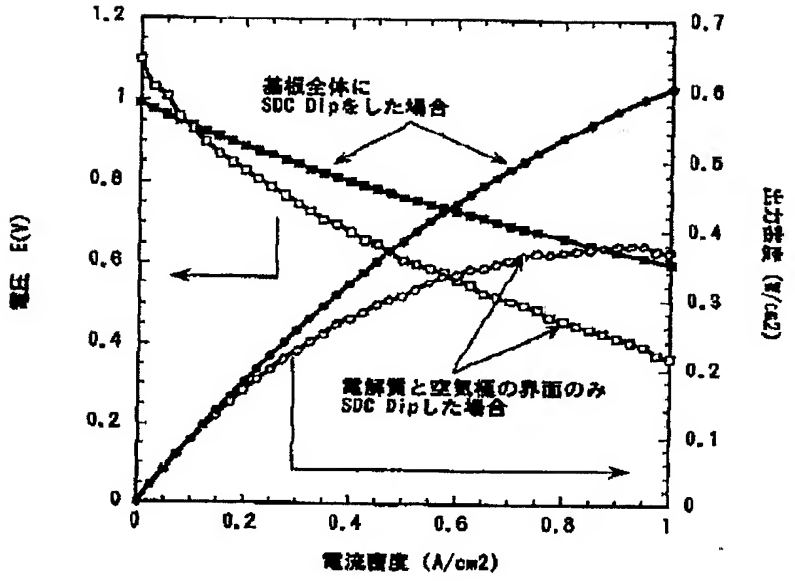

フロントページの続き

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HH05
5H026 AA06 BB04 EE13 HH05

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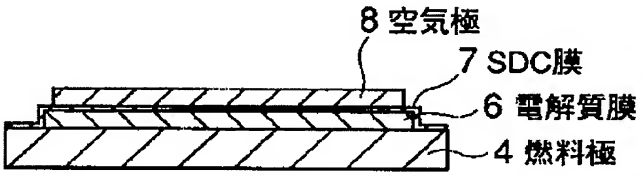
CLAIMS

[Claim(s)]
[Claim 1] Use a fuel electrode as a substrate, form an electrolyte membrane on this fuel electrode, and an air pole is formed on this electrolyte membrane. In the cell of the solid oxide fuel cell which supplies oxidant gas to said air pole, supplies fuel gas to said fuel electrode, is made to generate electromotive force among both, and obtains power between said electrolyte membranes and said air poles -- the film (F -- calcium --) of Ce1-X FX O (2-delta) The cell of the solid oxide fuel cell which is any one or two combination or more of Y, Sm, Gd, La, Mg, Sc, Nd, Yb, Pr, Pb, Sr, Eu, Dy, Ba, and Be, and was characterized by forming 0<=x<=0.50.
[Claim 2] The cell of the solid oxide fuel cell according to claim 1 characterized by forming the film of said Ce1-X FX O (2-delta) in the whole front face of said fuel electrode.
[Claim 3] The film of said Ce1-X FX O (2-delta) is the cell of the solid oxide fuel cell according to claim 1 or 2 characterized by being the Seria film which doped Samaria.
[Claim 4] Said electrolyte membrane is the manufacture approach of the cell of a solid oxide fuel cell given in any 1 term of claims 1-3 characterized by forming in said fuel electrode using print processes.
[Claim 5] Said print processes are the manufacture approaches of the cell of the solid oxide fuel cell according to claim 4 which is screen printing.

[Translation done.]

Drawing selection Representative drawing



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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] This invention relates to the cell of the solid oxide fuel cell which raised especially the generation-of-electrical-energy engine performance about the cell of the solid oxide fuel cell of the supporting lamella mold which constituted the fuel electrode as a base material.
[0002]
[Description of the Prior Art] The cell of a solid oxide fuel cell prepares an air pole in one electrolytic field, the fuel electrode is prepared in the field of another side, and two or more laminatings of such a cell are carried out, oxidant gas is supplied to an air pole, it supplies fuel gas to a fuel electrode, and the solid oxide fuel cell is generating electromotive force.
[0003] Next, the manufacture approach of the supporting lamella-type cell using a dip method is explained using the flow chart shown in drawing 12 .
[0004] Temporary quenching of the fuel electrode (Green) which carried out push harder shaping of the raw material of a powder-like fuel electrode with a press at the predetermined configuration (T1), and fabricated it first is carried out with an electric furnace etc. for about 100 hours, and it considers as a porous body (T2). Next, the fuel electrode which carried out temporary quenching is dipped into the electrolyte slurry which made the electrolytic raw material the shape of a slurry, and an electrolyte raw material is made to adhere to (T3) and the whole front face of a fuel electrode thinly. if an electrolyte slurry is made to adhere, an electrolyte slurry will be dried moderately -- making -- (T four) -- dip a fuel electrode into an electrolyte slurry again, an electrolyte raw material is made to adhere to a front face, and it dries again. Repeatedly, if an electrolyte membrane is formed in the front face of a fuel electrode at predetermined thickness, it will put into a furnace and adhesion / desiccation activity of such an electrolyte raw material will be calcinated, until an electrolyte raw material serves as predetermined thickness (about 7 times) (T5).
[0005] Next, an electrolyte membrane is ground, the unnecessary electrolyte membrane formed in the perimeter of a fuel electrode is removed, and a predetermined configuration is made (T6). And it was calcinating by preparing an air pole on an electrolyte membrane (T7) (T8).
[0006] Thus, conventionally, electric resistance reduced resistance for the high electrolyte membrane as a thin film of 10 - 10 micrometers of numbers, made operating temperature of a cell low, and was raising cost, heat mechanical dependability, etc. of a cell of a solid oxide fuel cell.
[0007]
[Problem(s) to be Solved by the Invention] However, a solid oxide fuel cell needs to attain a miniaturization and a high increase in power, and the cell is asked for the higher generation-of-electrical-energy engine performance in recent years. For example, the electric resistance between an electrolyte membrane, an air pole, or an electrolyte membrane and a fuel electrode is reduced more, and realizing the higher generation-of-electrical-energy engine performance is called for.
[0008]
[Means for Solving the Problem] In order to solve the above-mentioned technical problem, the cell consisted of this inventions as follows.
[0009] namely, between an electrolyte membrane and air poles -- film (F -- calcium --) of Ce1-X FX O (2-delta), such as a layer (film) of SDC (Seria which doped Samaria) It was any one or two combination or more of Y, Sm, Gd, La, Mg, Sc, Nd, Yb, Pr, Pb, Sr, Eu, Dy, Ba, and Be, and 0<=x<=0.50 was formed and the cell was constituted.
[0010] The method of application was the phase in which the electrolyte membrane was formed on the fuel electrode, and we applied the slurry of SDC etc. on the electrolyte membrane, and decided to form the after air pole on an

electrolyte membrane. Thereby, the electric resistance between an electrolyte membrane and an air pole can be reduced, and a cell with the high generation-of-electrical-energy engine performance can be obtained. Although what is necessary is just to apply the SDC film etc. to the field by the side of an electrolyte membrane at least, it may be applied to the fuel electrode front face of the rear face of the field in which the electrolyte membrane was formed.
[0011]
[Embodiment of the Invention] One example of the cell concerning this invention is explained.
[0012] A cell 2 is shown in drawing 1 . Have formed the electrolyte membrane 6 in the front face of the fuel electrode 4 as a base material, the SDC film 7 is made, as for a cell 2, to intervene on the front face of an electrolyte membrane 6 further, and the air pole 8 is formed. This cell 2 is pinched with the alloy separator 30 and the separator 34 which consists of a ceramic manifold 32, as shown in drawing 10 , the laminating of a separator 34 and the cell 2 is carried out suitably, and the solid oxide fuel cell 1 is constituted. A solid oxide fuel cell 1 generates electromotive force, when fuel gas is supplied to a fuel electrode 4 and it supplies oxidant gas to an air pole 8 in predetermined conditions (for example, temperature of 750 degrees C etc.).
[0013] Next, the manufacture approach of a cell 2 is explained using the flow chart of drawing 7 . First, a powder-like raw material is fabricated in a predetermined configuration, and the fuel electrode 4 as a base material is formed (S1). The raw materials of a fuel electrode 4 are nickel and the cermet of yttria stabilized zirconia (YSZ), knead a raw material with a water-soluble binder, for example, polyvinyl alcohol, and fabricate it in slight push hardness with press equipment (not shown) etc. The fuel electrode 4 fabricated in the predetermined configuration is shown in drawing 3 . Specified quantity content of the ostomy agent (not shown) has been carried out at the raw material of a fuel electrode 4, and many holes will be formed in the interior of a fuel electrode 4 if an ostomy agent is burned down by baking mentioned later.
[0014] The non-calcinated fuel electrode 4 fabricated by press equipment is arranged in the condition as it is at a coater 18 (refer to drawing 2), and the electrolyte slurry 24 is applied to a front face (S2). The electrolyte slurry 24 kneads the raw material of the electrolyte (electrolyte membrane 6) which consists of YSZ and the binder of nonaqueous solubility, for example, a polyvinyl butyral, and has set it as predetermined viscosity. In addition, as a binder, there are methyl cellulose, polyethylene, sodium polyacrylate, gum arabic, etc. in addition to the above.
[0015] As shown in drawing 2 , a coater 18 is a printing machine which prints with the so-called screen printing, and the mold of a configuration equal to an electrolyte membrane 6 is formed in the screen version 20. If a fuel electrode 4 is arranged to the position of a coater 18, the electrolyte slurry 24 will be applied to the top face of a fuel electrode 4 through a mold by moving a squeegee 22 along with the screen version 20 (S2). If the electrolyte slurry 24 is applied to a predetermined configuration, an electrolytic front face will be dried suitably. Desiccation should just be extent which can apply the electrolyte slurry 24 in piles on the electrolyte slurry 24 which did not need to be dried completely and applied the electrolyte slurry 24. The fuel electrode 4 with which the electrolyte membrane 6 was formed in the front face is shown in drawing 4 .
[0016] If the electrolyte slurry 24 is dried moderately, the electrolyte slurry 24 will be applied in piles like the above, and it will be made to dry. And spreading of the electrolyte slurry 24 is repeated until the electrolyte slurry 24 becomes predetermined thickness. If the laminating of the electrolyte slurry 24 is carried out to predetermined thickness, it will co-sinter with a fuel electrode 4 (S3). (calcinate an electrolyte membrane 6 and a fuel electrode 4 together)
[0017] And SDC is applied to an electrolyte membrane 6 and the SDC film 7 is formed. SDC is Seria (Ce1-xSmxO (2-delta)) which doped Samaria, and particle size is x= 0.3 in about 0.1-5 micrometers. SDC distributes the powder to Ce sol, is mixed, forms an SDC slurry, and applies it to the thickness of 4 micrometers on the whole front face of an electrolyte membrane 6 with a dip method etc. (S4). The condition that the SDC film 7 was applied is shown in drawing 5 . Next, the applied SDC film 7 is calcinated at predetermined temperature (S5). If it calcinates, an air pole 8 is applied on an electrolyte membrane 6 through the SDC film 7 (S6), and the whole will be calcinated and it will be made to complete (S7). from the particle (LSCF-SDC) to which an air pole 8 has the presentation of Ce0.8 Sm 0.2O1.9 whose particle size in which mean particle diameter encloses La0.6Sr0.4Co0.8Fe 0.2O3 which is 0.60 micrometers, and the perimeter of this particle is 0.1 micrometers -- becoming -- Ce0.8 Sm 0.2O1.9 -- 0.5 - 60wt% -- it is contained. The whole cell 2 in which the air pole 8 was formed on the electrolyte membrane 6 is shown in drawing 6 .
[0018] In addition, an air pole 8 is O (C(A1-x Bx)1-y Dy) (3+delta). The particle which has a presentation, the particle (A -- La and Y --) which has the presentation of Ce1-X EX O (2-delta) Any one or two combination or more of Sm, Gd, Pr, and calcium, and B Sr, Any one or two combination or more, Ba and calcium, and C Mn, Co, Any one or two combination or more of Ce, and D Cr, nickel, Mg, Any one or two combination or more of Zr, Ce, Fe, and aluminum, and E calcium, Y, Sm, Gd, La, Mg, Sc, Nd, Yb, Pr, Pb, Sr, It is any one or two combination or more of Eu, Dy, Ba, and Be. The path of the particle to which, as for the particle which has the presentation of O (3+delta), a path has the

presentation of 0.1-20 micrometers and Ce1-X EX O (2-delta) that what is necessary is just to constitute from 0<=x<=0.50 and 0<=y<=0.50 (C1-y Dy) (A1-x Bx) should just be 0.1-5 micrometers.
[0019] furthermore, between an electrolyte membrane 6 and an air pole 8, it may not come out SDC film 7, and the film (F is any one or two combination or more of calcium, Y, Sm, Gd, La, Mg, Sc, Nd, Yb, Pr, Pb, Sr, Eu, Dy, Ba, and Be, and is 0<=x<=0.50) of Ce1-X FX O (2-delta) may be formed. Moreover, the particle size should just be about 0.1-2 micrometers. Furthermore, the ratio of the thickness of viewpoints, such as oxygen tension and a difference of the thermal expansion of each film, to the electrolyte membrane 6 and SDC film 7 grade should just be ten or more substantially.
[0020] Thus, by having formed the conductive high SDC film 7 between the electrolyte membrane 6 and the air pole 8, the electric resistance of the interface of an air pole 8 and an electrolyte membrane 6 is reduced, and the high generation-of-electrical-energy engine performance can be obtained. Moreover, by having formed the electrolyte membrane 6 using screen printing, irregularity is formed in a front face, the touch area between an electrolyte membrane 6 and an air pole 8 increases, and adhesion improves.
[0021] Furthermore, since the direct electrolyte slurry 24 can be applied to a fuel electrode 4, without being able to apply and form a predetermined configuration and the electrolyte membrane 6 of thickness in the fuel electrode 4 which is a base material simply and quickly, and carrying out temporary quenching of the fuel electrode 4 after fabricating the raw material of a fuel electrode 4, time and effort and cost are sharply reducible. Moreover, from passing the screen version 20 and applying the electrolyte slurry 24, moderate irregularity is formed and the good electrolyte membrane 6 can be formed.
[0022] moreover, a fuel electrode 4 and the electrolyte slurry 24 -- when the property of each binder, i.e., a binder, chooses the combination of water solubility or nonaqueous solubility suitably, after being able to adjust the condition of the interface formed among both at the time of applying the electrolyte slurry 24 to a fuel electrode 4 and calcinating, it is precise, and the good electrolyte membrane 6 with few impurities can be formed. Furthermore, the front face of an electrolyte membrane 6 and the interface of an electrolyte membrane 6 and a fuel electrode 4 can be made into desired structure by making it cooperate other than the combination of water solubility, nonaqueous solubility, etc., coming out, and choosing both binder suitably.
[0023] In addition, the SDC film 7 may be applied to the whole outside surface of a fuel electrode 4 and an electrolyte membrane 6 as shown in whole electrolyte membrane 6 not a front face but drawing 8 and drawing 9 . Moreover, the conventional air pole is sufficient as an air pole 8, and the manufacture approach which forms an air pole 8 on an electrolyte membrane 6 is also easy to come out of it as usual.
[0024] In addition, although [the above-mentioned example] an electrolyte slurry is applied and an electrolyte membrane is formed with screen printing, in this invention, not only screen-stencil but other print processes are sufficient, and an electrolyte membrane may be further formed with a dip method.
[0025] Moreover, the combination of not only the above-mentioned example but other classes is sufficient as the property of a binder.
[0026] The experimental result which starts this invention at example drawing 11 of an experiment is shown. The cell used for the experiment YSZ and an air pole for the cermet of nickel and YSZ, and an electrolyte An average of 0.6-micrometer O (Co(La1-xSrx)1-yFey) (3+delta) particle (x= 0.4, y= 0.2), [a fuel electrode] Where it constituted from a 0.1-micrometer Ce1-xSmxO (2-delta) particle (x= 0.2) and an electrolyte membrane is formed in a fuel electrode Another side prepared the SDC (Ce0.7Sm0.3O (2-delta)) film only between the electrolyte membrane and the air pole, and one side formed the air pole on the SDC film at the whole, respectively.
[0027] Supplied fuel gas and oxidant gas for these cells with the operating temperature of 750 degrees C, the generation of electrical energy was made to start, and the electrical potential difference to current density was measured. It turns out that there is little descent of an electrical potential difference even if current density rises, the high generation-of-electrical-energy engine performance is obtained by this, and a result with it better [to form the SDC film not only in between a fuel electrode and electrolyte membranes but in the reverse, i.e., front face of fuel electrode, side of an electrolyte membrane moreover] is obtained.
[0028]
[Effect of the Invention] according to the cell of this invention -- at least -- between an electrolyte membrane and air poles -- film (F -- calcium --) of Ce1-X FX O (2-delta), such as SDC film By being any one or two combination or more of Y, Sm, Gd, La, Mg, Sc, Nd, Yb, Pr, Pb, Sr, Eu, Dy, Ba, and Be, and having formed 0<=x<=0.50 The electric resistance of an electrolyte membrane and an air pole can be reduced, and the cell of the high generation-of-electrical-energy engine performance can be obtained.

[Translation done.]

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]
[Drawing 1] It is drawing showing the cell concerning this invention.
[Drawing 2] It is drawing showing a coater.
[Drawing 3] It is drawing showing a fuel electrode.
[Drawing 4] It is drawing showing the fuel electrode in which the electrolyte membrane was formed.
[Drawing 5] It is drawing showing the fuel electrode in which the SDC film was formed.
[Drawing 6] It is drawing showing a cell.
[Drawing 7] It is drawing showing the procedure of the manufacture approach concerning this invention.
[Drawing 8] It is the sectional view of an electrolyte membrane and a fuel electrode in which the SDC film was formed.

[Drawing 9] It is the sectional view showing the cell in which the SDC film was formed.
[Drawing 10] It is drawing showing a solid oxide fuel cell.
[Drawing 11] It is drawing showing an experimental result.
[Drawing 12] It is drawing showing the procedure of the conventional manufacture approach.
[Description of Notations]
2 Cell
4 Fuel Electrode
6 Electrolyte Membrane
7 SDC Film
8 Air Pole
18 Coater
20 The Screen Version
22 Squeegee
24 Electrolyte Slurry
30 Alloy Separator
32 Ceramic Manifold
34 Separator

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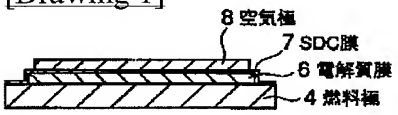
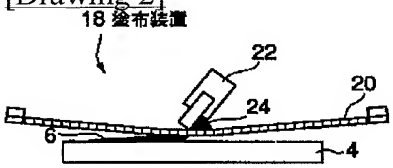
DRAWINGS

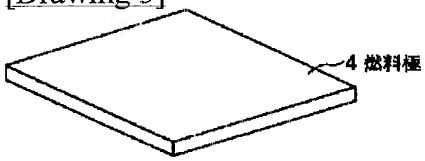
[Drawing 1]



[Drawing 2]

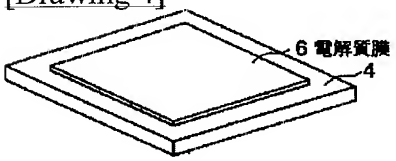


[Drawing 3]

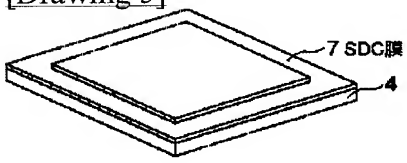


[Drawing 8]

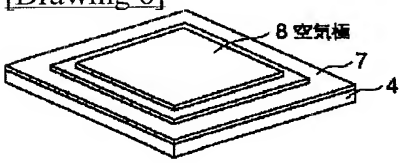
[Drawing 4]



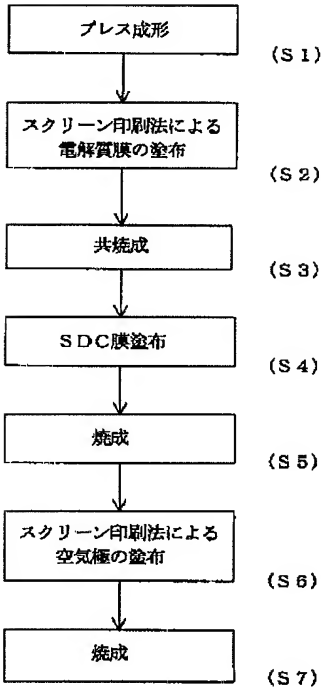
[Drawing 5]



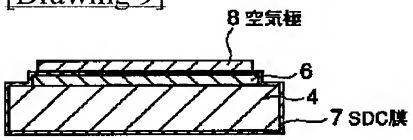
[Drawing 6]



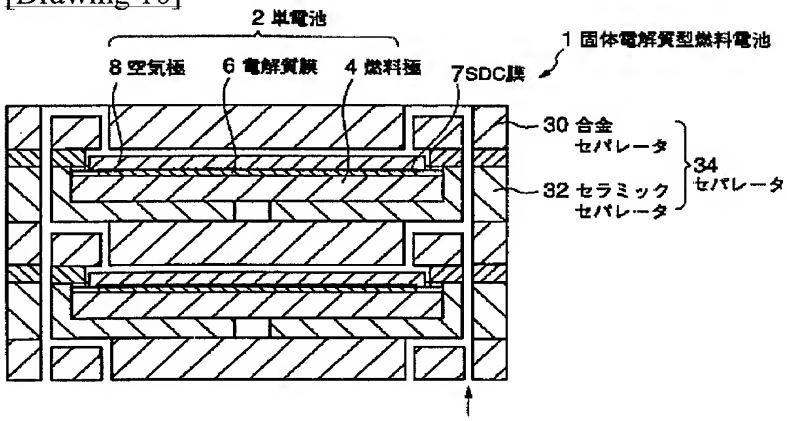
[Drawing 7]



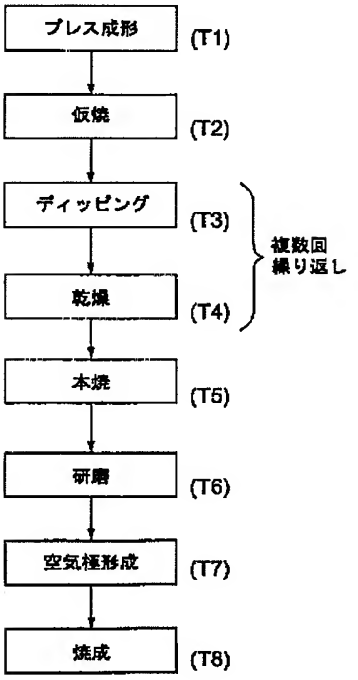
[Drawing 9]



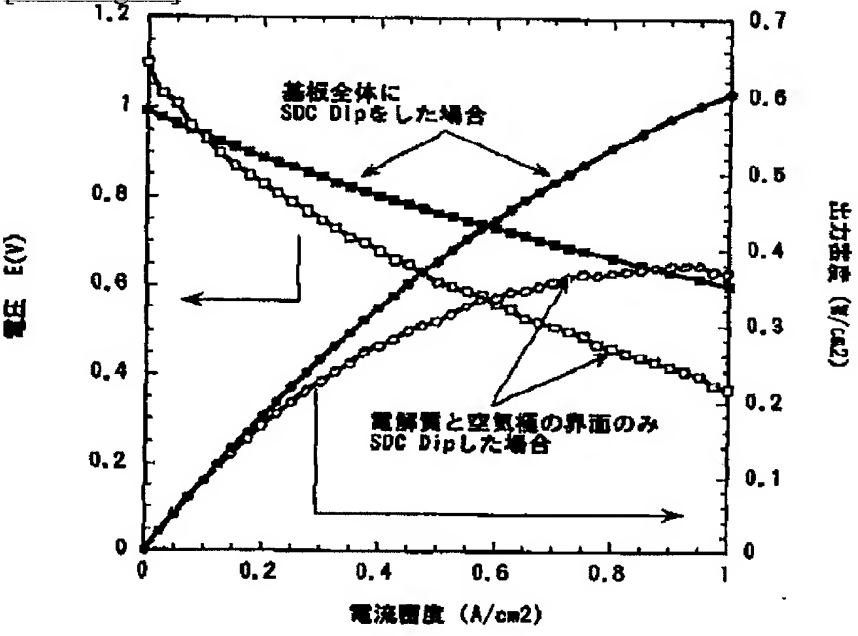
[Drawing 10]



[Drawing 12]



[Drawing 11]



[Translation done.]